MICROSTRUCTURE STUDIES OF POLYCRYSTALLINE REFRACTORY OXIDES
QUARTERLY PROGRESS REPORT NO. 2

Prepared by

T. Vasilos
R. M. Spriggs
J. B. Mitchell

RAD-SR-63-29
Prepared under U. S. Navy, Bureau of Weapons
Contract Now 62-0648c

14 February 1963

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RESEARCH AND ADVANCED DEVELOPMENT DIVISION
AVCO CORPORATION
Wilmington, Massachusetts

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APPROVAL

Charles Spencer, Manager
Materials Department

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ABSTRACT

Transverse bend strength and elastic modulus determinations made of fine-grained (1 to 2 micron) dense, pure Al_2O_3 and MgO specimens as a function of temperature (up to 1350°C) revealed values higher than those obtained by other investigators for these oxides in more porous form and of larger grain sizes. Studies of the grain growth kinetics of alumina and magnesia were conducted in order to obtain information to enable preparation of specimens with desired larger grain sizes for subsequent thermomechanical testing. Based on observations of the fracture modes exhibited by alumina and magnesia as a function of temperature, it was suggested that anelastic deformation or possible plastic flow in the so-called "equicohesive" temperature range may influence the mode of fracture. By analogy with findings in metals systems, it was hypothesized that the apparent transition from transgranular to intergranular fracture might occur below some critical stress rather than above some critical temperature.

CONTENTS

ILLUSTRATIONS

I. INTRODUCTION

This is the second quarterly progress report on microstructure studies of polycrystalline refractory oxides. The overall objective of this project is to determine the effects of microstructure on the elevated-temperature, mechanical-strength properties of selected ceramic-oxide refractory materials. Primary emphasis is currently being placed on the effect of grain size on the elevated-temperature transverse bend strength and elastic modulus of pure, single-phase alumina and magnesia.

During the period covered by this report, transverse bend strength and elastic modulus determinations were made on fine-grained (1- to 2-micron) dense, pure Al_2O_3 and MgO as a function of temperature. In addition, preliminary studies were conducted to determine the kinetics of grain growth of these materials in order to obtain the desired larger grain sizes for this investigation. Finally, some observations were made of the modes of fracture, exhibited by the fine-grained alumina and magnesia as a function of temperature. The influence of anelastic deformation or possible plastic flow on the mode of fracture in the "equicohesive" temperature range has been discussed.

In this report, the bend strength and elastic modulus values obtained for fine-grained alumina and magnesia are compared with earlier data on these materials reported by Schwartz[1] and Coble and Kingery[2]. It is recognized that several other investigators (see, for example, references 3 through 6) have also studied the room and elevated temperature bend strength and elastic modulus behavior of these materials with varying microstructures, purities, testing conditions, etc. However, data were not available for simultaneous measurements of strength and modulus on the same, pure, highly dense specimens as a function of grain size and temperature. Thus, the data of Schwartz and Coble and Kingery proved to be most suitable for comparison with the present results.

Possible effects due to factors such as surface conditions continue to be under close surveillance during this study. For example, surface-roughness measurements made on various Al_2O_3 and MgO specimens before and after elevated-temperature testing have revealed no measurable changes in surface condition during testing.

Future plans call for completing the bend strength and elastic modulus determinations as a function of temperature of alumina and magnesia specimens which have received thermal treatments to cause varying amounts of grain growth to occur.

II. GRAIN GROWTH STUDIES

In order to obtain the desired grain sizes for this investigation, several preliminary studies were made to determine the kinetics of grain growth of the alumina and magnesia materials. Figure 1 plots log grain size versus log time for the grain growth of Al_2O_3 and MgO at various temperatures. The grain-size determinations were made with an optical microscope using a filar eyepiece. In the early stages of grain growth, the grain sizes were at the limit of resolution of the microscope and considerable error resulted from an inability to resolve small individual grains. Accurate determinations of the smaller grain sizes are now being made from electron-microscope replicas of the specimens. The curves shown in figure 1 are still useful in determining the time and temperature to obtain a larger grain size. Specimens are now being heat-treated to obtain the larger grain sizes for testing. Examples of the microstructures obtained during grain growth of Al_2O_3 and MgO are shown in figures 2 and 3, respectively.

The rather slow grain growth rate obtained in Al_2O_3 has led to efforts to enhance the growth by heating in a hydrogen atmosphere with a subsequent treatment in air. These experiments are now being carried out.

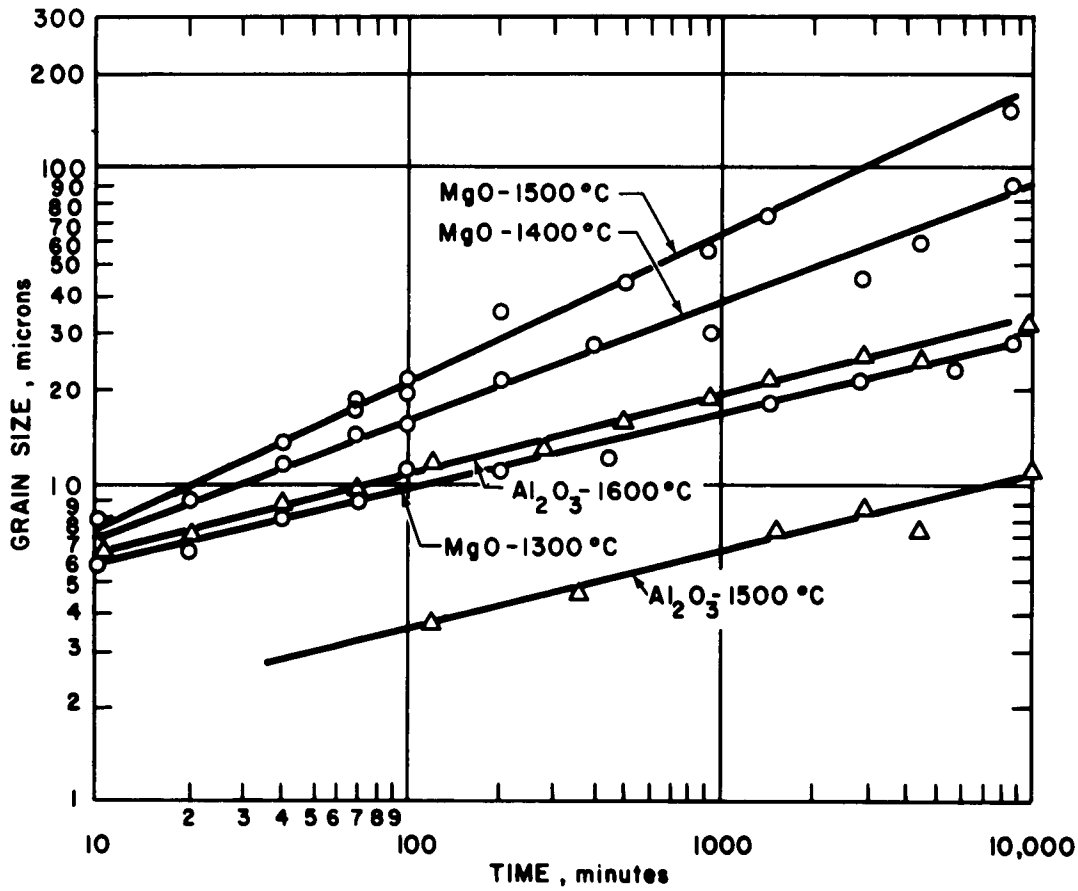
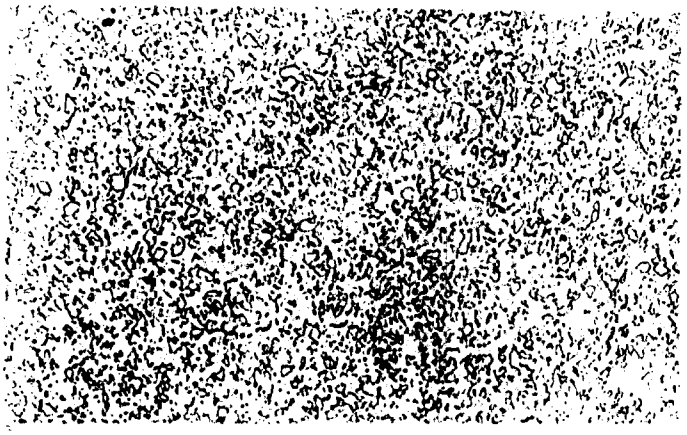


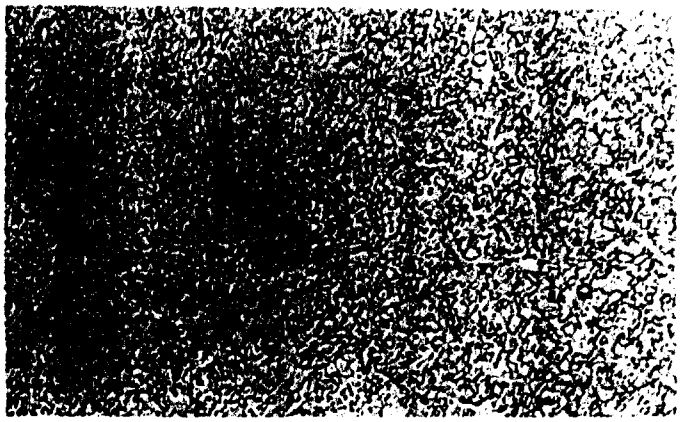
Figure 1 LOG GRAIN SIZE VERSUS LOG TIME FOR GRAIN GROWTH OF MgO AND Al_2O_3

63-1548



2989A 250X

6 HOURS, 4 MICRONS

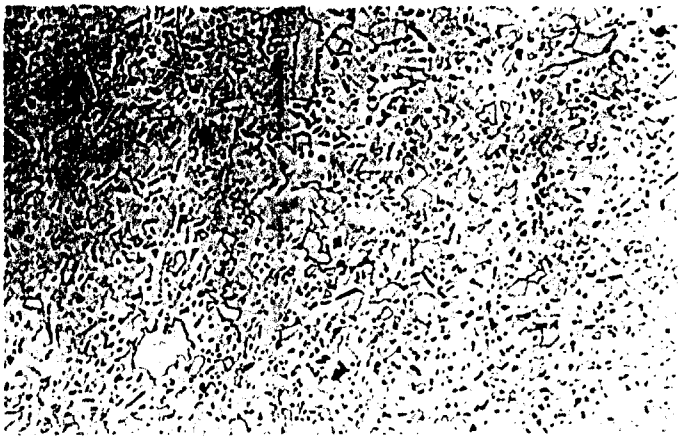


2989C 250X

48 HOURS, 8 MICRONS

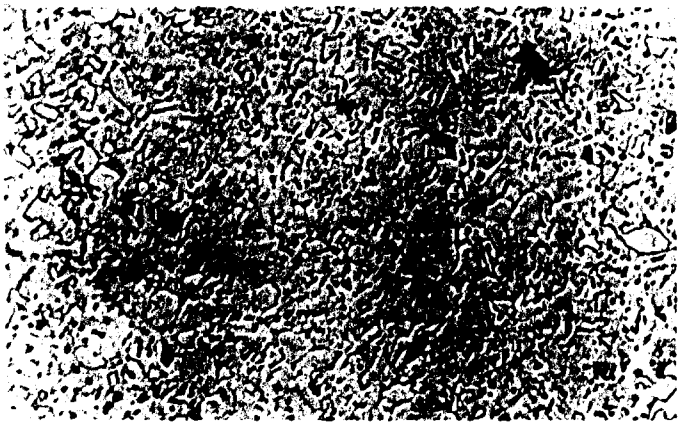
2989F 250X

168 HOURS, 12 MICRONS



2989G 250X

192 HOURS, 16 MICRONS



2989H 250X

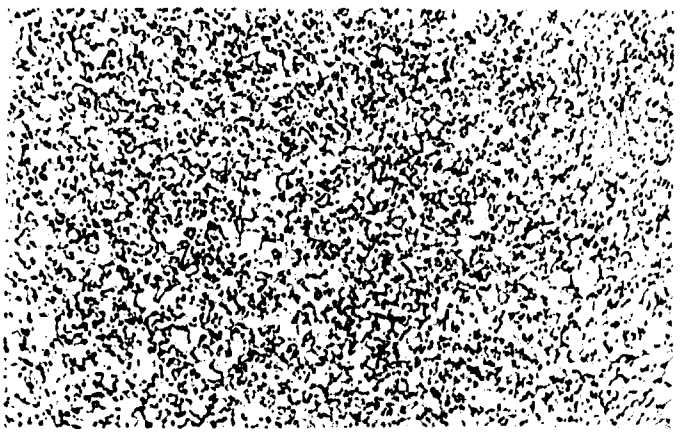
216 HOURS, 18 MICRONS

2989Q 250X

312 HOURS, 27 MICRONS

Figure 2 TYPICAL MICROGRAPHS OF Al_2O_3 SPECIMENS HEAT-TREATED AT 1500°C TO CAUSE GRAIN GROWTH TO OCCUR

63-1553

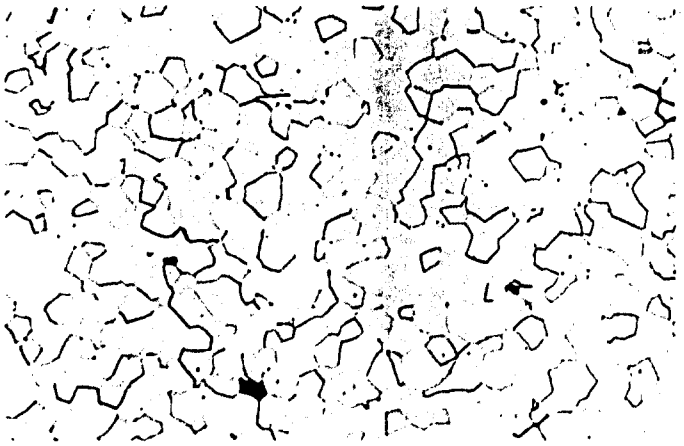


3048 250X

AS PREPARED, 2 MICRONS

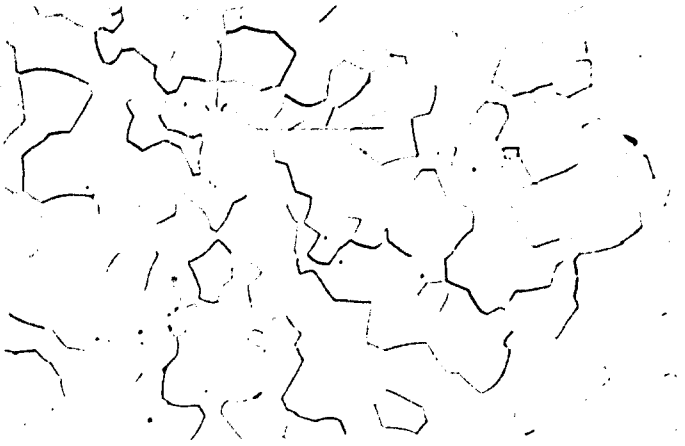
3048E 250X

100 MINUTES, 1500°C-5 MICRONS



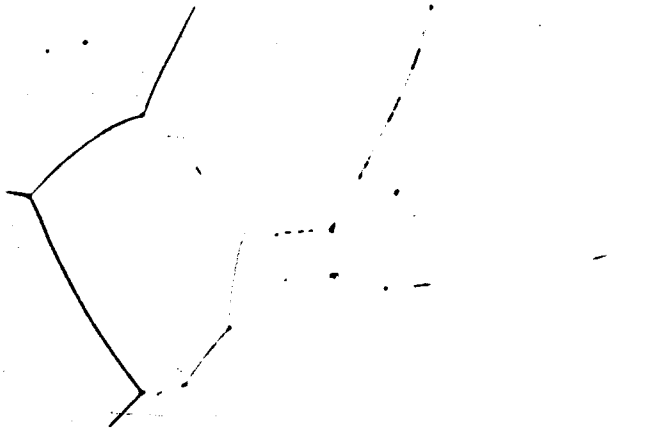
3045 250X

10 MINUTES, 1600°C-12 MICRONS



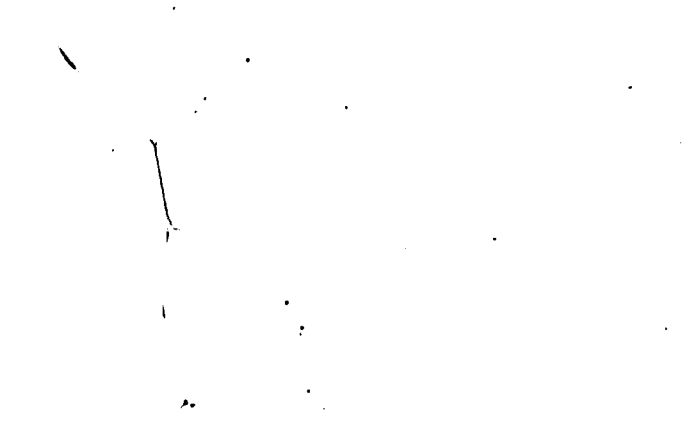
3045D 250X

100 MINUTES, 1600°C-20 MICRONS



3045G 250X

1420 MINUTES, 1600°C-38 MICRONS



3045H 250X

4320 MINUTES, 1600°C-72 MICRONS

Figure 3 TYPICAL MICROGRAPHS OF MgO SPECIMENS HEAT-TREATED TO CAUSE GRAIN GROWTH TO OCCUR

63-1551

III. MECHANICAL PROPERTIES DETERMINATIONS

The initial tests of elastic modulus in transverse bending yielded erratic results. It was found that the correction for apparatus deflective at the test temperature changed in an unpredictable manner with each application of the load, due to thermal and stress effects on the apparatus parts. This problem was eliminated by modifying the apparatus so that the deflection-sensing instrument (linear variable differential transformer) measured only specimen deflection with respect to the lower knife edges, eliminating the need of correcting for apparatus deflection.

Figure 4 shows typical load-deflection curves obtained for transverse bending of fine-grained (1- to 2-micron) Al_2O_3 and MgO at various test temperatures. Elastic modulus and modulus of rupture values were calculated with the conventional beam-deflection formulas in four-point loading:

$$E_{t.b.} = \frac{P}{y}\left[\frac{a}{4bd^3}(3l^2 - 4a^2)\right]$$

$$\sigma_{t.b.} = \frac{3Pa}{bd^2}$$

where

P = load, pounds

l = span, inches

b = specimen width, inches

d = specimen depth, inches

y = specimen deflection, inches

a = distance from point of load to point of reaction, inches.

The ratio P/y was determined from the linear portion of the load-deflection curve. The elastic modulus and modulus of rupture of fine-grained Al_2O_3 and MgO are shown as a function of test temperature in figures 5 and 6, respectively. Also plotted for comparison are the data of Schwartz[1] and Coble and Kingery[2]. The curves of elastic modulus are in general agreement with the trend of the data presented by the above investigators. Both the alumina and magnesia exhibited higher elastic moduli and showed stronger temperature dependence between 30 and 400°C and between 700 and 1000°C than the materials used by Schwartz and Coble. It is not yet clear whether this effect was due principally to a decreased grain size or a decrease in porosity. Coble's

alumina had a grain size of 25 microns and a minimum of 10 percent porosity. The alumina used by Schwartz had 4 percent porosity and the magnesia 11 percent porosity. The grain size of Schwartz's materials was not known.

While several other investigators have studied microstructure effects on the elevated-temperature mechanical properties of refractory oxides,[3-6] the data of Schwartz and Coble and Kingery proved to be most suitable for comparison with the present results.

Comparison of the transverse bend strengths of Al_2O_3 and MgO with those of Schwartz showed a significant increase in strength which was probably due to a combination of higher density and smaller grain size in the present materials. However, an exact quantitative comparison of the strength values is not justified since the specimen cross section and gage lengths used by Schwartz differed for those used in the present investigation.

The large degree of scatter in the reported data was principally due to differences in fabrication conditions, which were initially varied to achieve optimum density, grain size, and strength in the specimens. Specimens fabricated under the same conditions of temperature, pressure, and time exhibited relatively little scatter in mechanical properties. Specimens fabricated under slightly different conditions, e.g., relatively higher hot-pressing temperature but for shorter time, although having the same apparent density and grain size, exhibited significant differences in transverse bend strength and elastic modulus. It is not, at present, understood how these variations in fabrication conditions affect the mechanical properties. Subsequent specimens for this investigation, approximately 400 of alumina and 300 of magnesia, were fabricated under identical conditions. Testing of specimens having a grain size of approximately 50 microns is now being carried out.

Testing of surface conditions of the specimens before and after high-temperature mechanical testing was accomplished by running surface-roughness tests on a Talysurf machine. The average deviation from a reference centerline (centerline average, CLA) was taken as the measure of surface condition. No change was found to occur in the surface conditions of the specimens during testing. The average surface roughness was 14 to 22 μ inches.

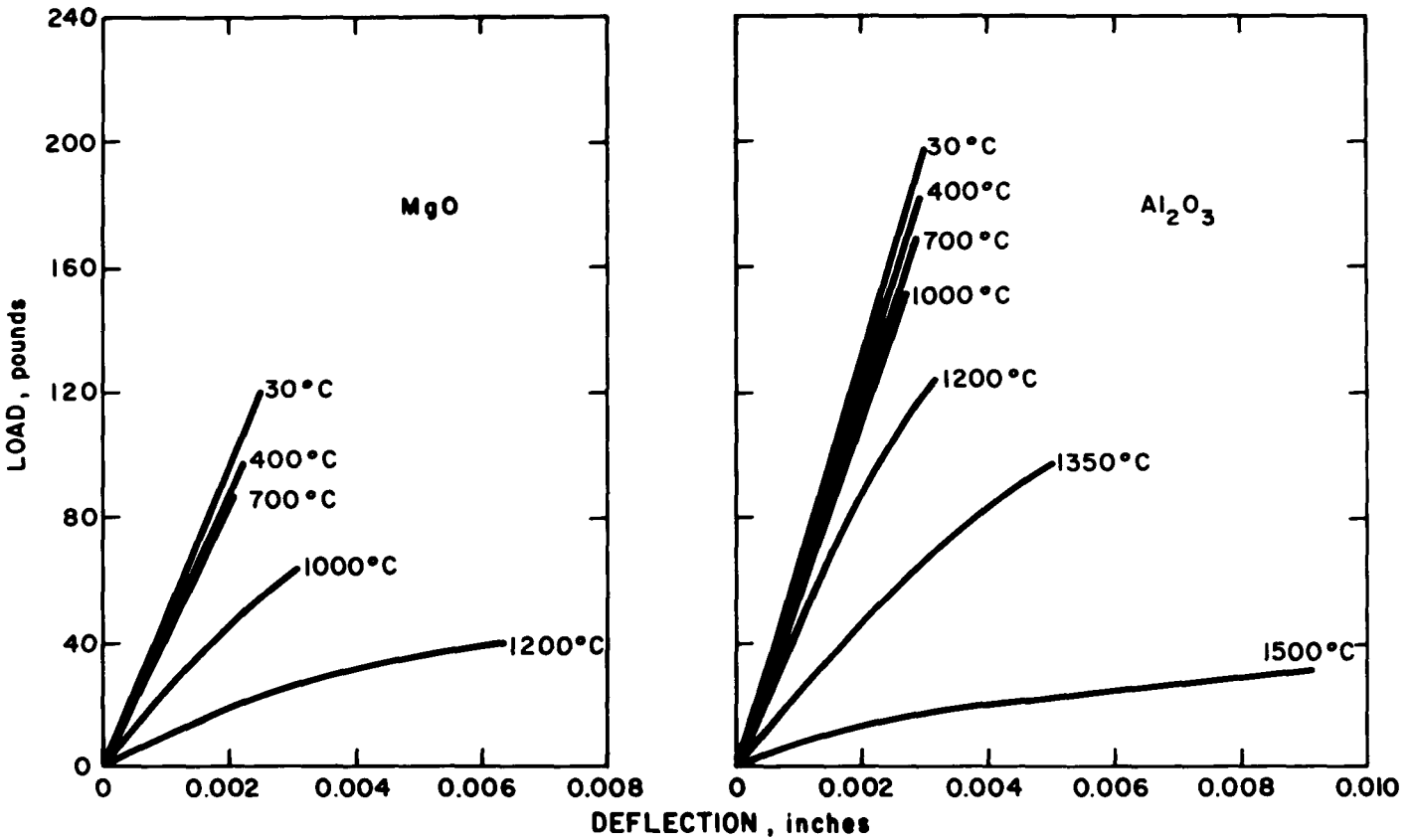


Figure 4 LOAD VERSUS DEFLECTION FOR TRANSVERSE BENDING AT VARIOUS TEST TEMPERATURES
63-1547

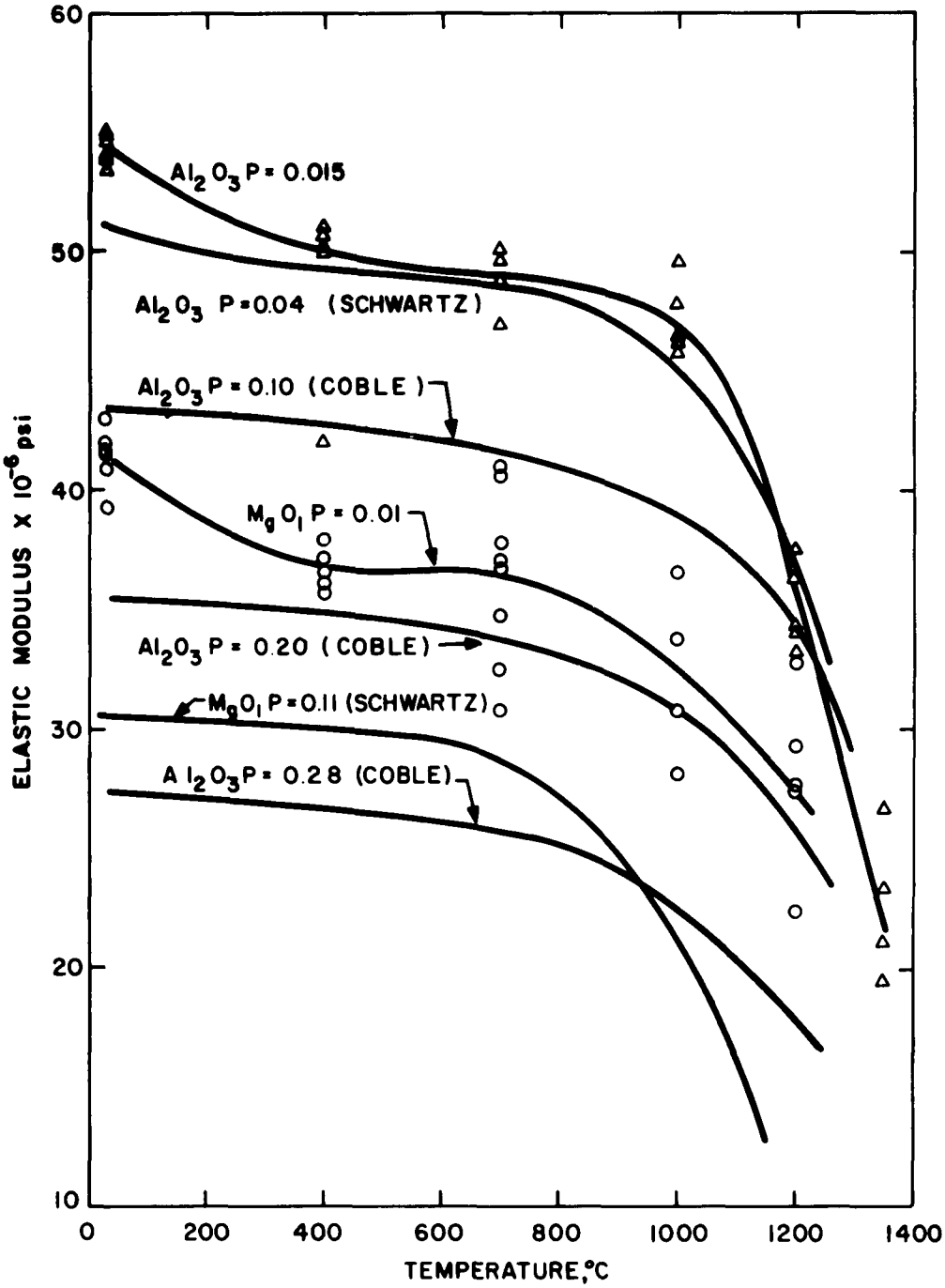


Figure 5 MODULUS OF ELASTICITY VERSUS TEMPERATURE
65-1546

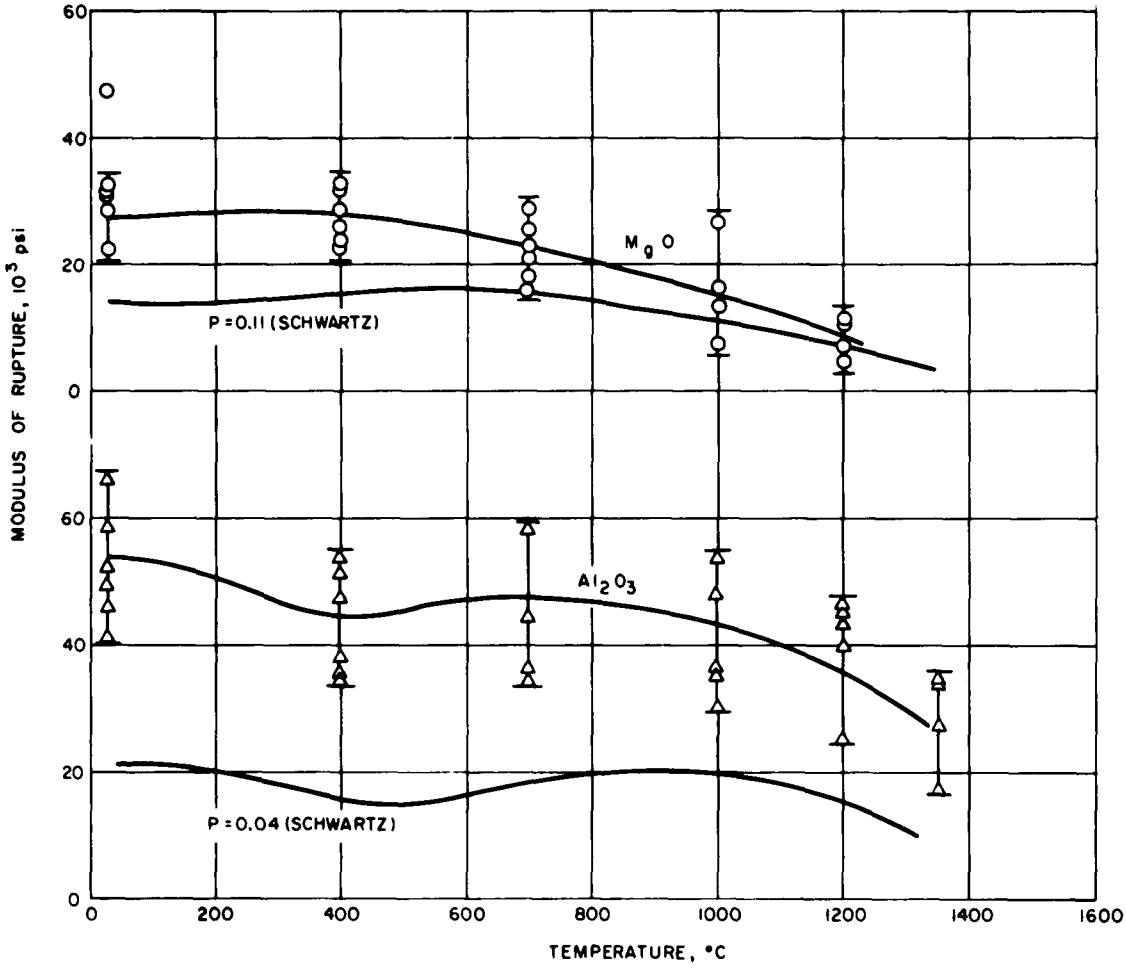


Figure 6 MODULUS OF RUPTURE VERSUS TEMPERATURE
63-1549

IV. OBSERVATIONS ON FRACTURE MODES

Typical fracture surfaces exhibited by Al_2O_3 and MgO specimens broken at various test temperatures are shown in figure 7. The alumina specimens exhibited very rough and irregular fracture surfaces up to 1200°C and magnesia up to 700°C. Specimens fractured at room temperature frequently broke into three or four pieces in the local region of the fracture. At higher temperatures, the fractures became smooth and regular in appearance as though sliced normal to the tensile axis.

Figures 8 and 9 are electron fractographs of the fractured surfaces of several Al_2O_3 and MgO specimens. These fractographs revealed a combination of intergranular and transgranular fracture in both Al_2O_3 and MgO. The principal mode of fracture in Al_2O_3 at test temperatures up to 1000°C and in MgO up to 700°C appeared to be transgranular. Intergranular fracture was also observed in the microstructure in this temperature range. Fractographs of specimens tested at higher temperatures revealed fracture to be predominantly intergranular. Fracture in Al_2O_3 specimens tested at 1350°C and in MgO specimens tested at 1200°C appeared to be entirely intergranular.

These observations indicated that the change in macroscopic fracture characteristics exhibited in Al_2O_3 and MgO over the so-called "equicohesive" temperature range (see, for example, reference 7) results from an increase in the ratio of intergranular to transgranular fracture with increasing test temperature.

It is of interest to note that it is in these temperature ranges that the specimens begin to exhibit yielding and a nonlinear load-deflection behavior prior to fracture. It is suggested that this anelastic deformation or possible plastic flow may influence the mode of fracture of these materials. Strain damage in and about the grain-boundary region might lead to intergranular fracture. Chang and Grant[8] found that stress concentrations at the junction of grains where grain-boundary sliding had occurred often resulted in the formation of cracks. They found that cracks spread from one triple point to another along a more or less direct path in the plane of the boundary. McLean,[9-12] in a series of unique experiments showed that creep deformation in polycrystalline metal aggregates occurred by means of migration of dislocations (resulting in slip and subboundary formation) and by means of grain-boundary sliding. Under a given stress, the ratio of the fraction of creep strain arising from grain-boundary shearing to total creep strain $\left(\frac{E_{g.b.}}{E_t}\right)$ remained essentially constant. This ratio was found to increase as the stress decreased. Using McLean's technique on creep in polycrystalline aluminum, Fazan, Sherby, and Dorn[13]

confirmed McLean's observations and showed that the ratio $\frac{E_{g.b.}}{E_t}$ for a given stress was independent of temperature. As suggested by Dorn,[14] these results indicated that grain-boundary shearing might be attributed to localized crystallographic mechanisms of deformation in the region of the grain boundary rather than a process such as viscous shearing. Since the strain arising from grain-boundary shearing is a function of the total strain for a given stress, independent of temperature, the localized strain damage in and around the grain-boundary region such as might lead to intergranular fracture should also depend on the total strain independent of temperature. McLean's data which showed that the ratio $\frac{E_{g.b.}}{E_t}$ increases with decreasing stress suggests that the strain damage becomes more and more concentrated in the vicinity of the grain boundary as the stress is decreased.

While similar observations of structural changes attending deformation in fully dense polycrystalline refractory oxides have not been made, it is reasonable to assume that the same relationships might be evident in these materials. Such observations in these materials would indicate that the apparent transition from transgranular to intergranular fracture might occur below some critical stress rather than above some critical temperature.

A complimentary study of phenomenological and structural changes attending creep deformation in fully dense MgO and Al_2O_3 would elucidate possible relationships between deformation, microstructure, and mechanical properties of refractory oxides.

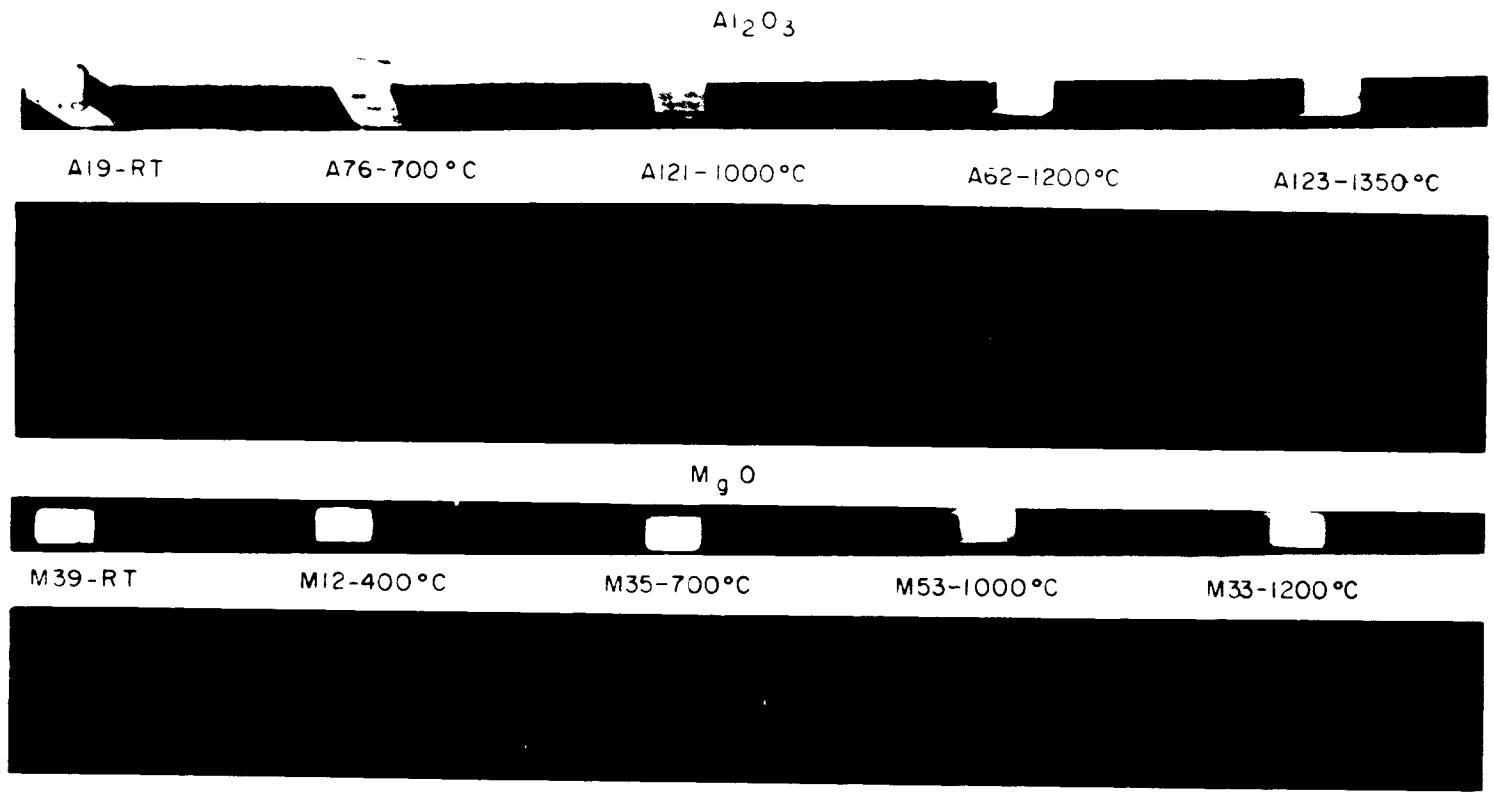
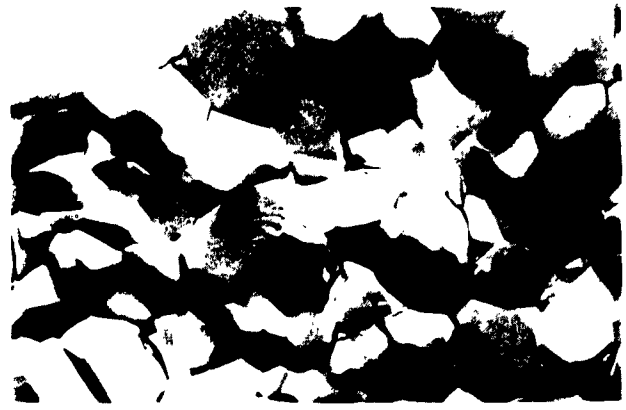


Figure 7 TYPICAL FRACTURE SURFACES EXHIBITED BY SPECIMENS OF Al_2O_3 AND MgO BROKEN IN TRANSVERSE BENDING AT VARIOUS TEST TEMPERATURES
63-1550

62BD22 6900X

ROOM TEMPERATURE, 2.1 MICRONS



62BD16 6900X

400 °C, 1.4 MICRONS

62BJ15 6600X

700 °C, 1.7 MICRONS

62BJ16 13,000X

700 °C, 1.7 MICRONS

62BJ5 6600X

1350 °C, 1.5 MICRONS

62BJ6 13,800X

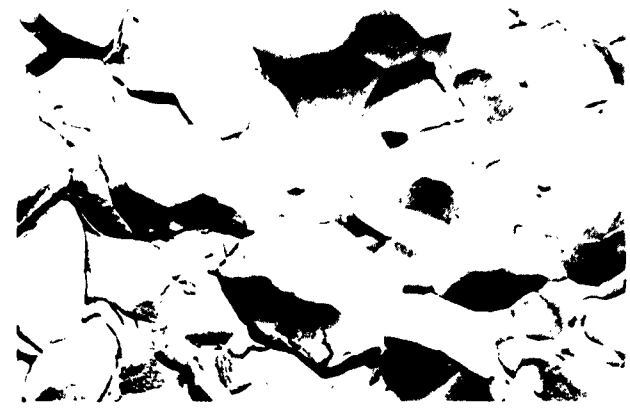
1350 °C, 1.5 MICRONS

Figure 8 ELECTRON FRACTOGRAPHS OF Al_2O_3 SPECIMENS BROKEN IN TRANSVERSE BENDING AT VARIOUS TEMPERATURES

63-1552

62BDIO 6900X

ROOM TEMPERATURE 1.4 MICRONS



62BD7 6900X

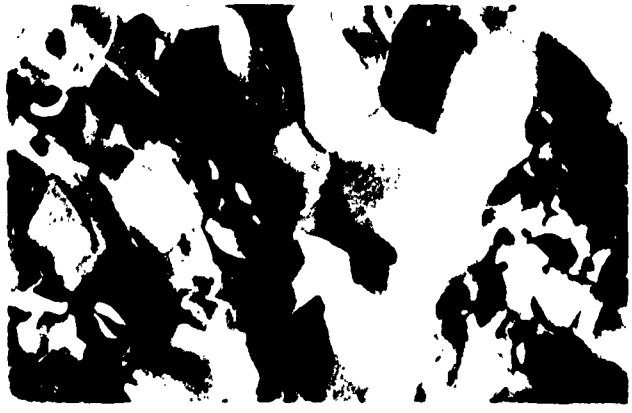
400 °C, 1.3 MICRONS

62BII0 6600X

700 °C, 1.8 MICRONS

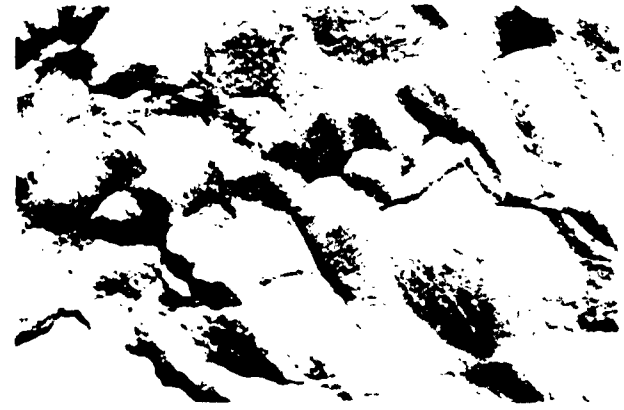
62BII4 13,800

700 °C, 1.8 MICRONS



62BI0 6600X

1200 °C, 2.0 MICRONS



62BI5 13,800X

1200 °C, 2.0 MICRONS

Figure 9 ELECTRON FRACTOGRAPHS OF MgO SPECIMENS BROKEN IN TRANSVERSE BENDING AT VARIOUS TEMPERATURES

63-1254

V. FUTURE WORK

The necessary specimens of fine-grained, dense, pure Al_2O_3 and MgO to cover the desired larger grain-size ranges and testing temperatures have been fabricated and machined. Subsequent thermal treatments are being employed to achieve the larger grain sizes up to 300 to 500 microns. During the remainder of the project, it is planned to complete the strength and modulus determinations of these larger grain-size specimens as a function of temperature. Testing of specimens having a grain size of approximately 50 microns is now in progress.

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